

JAPANESE

[JP,2002-241411,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE
INVENTION TECHNICAL PROBLEM MEANS EXAMPLE

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]When this invention is excellent in a warm water-proof adhesive property and leaving stability and is coat-ized further, it relates to the process of the vinylester resin emulsion which is excellent also in film formability and transparency.

[0002]

[Description of the Prior Art]Conventionally polyvinyl alcohol (it may be hereafter written as PVA) An ethylenic unsaturated monomer, It is widely used as protective colloid for emulsion polymerizations of the vinyl ester system monomer represented by especially vinyl acetate. The vinyl ester system aqueous emulsion produced by carrying out an emulsion polymerization using this as protective colloid For papers, It is widely used in fields, such as the various binders the various adhesives the object for woodwork, for plastics, etc., the object for impregnated papers, for nonwoven products, etc., admixture, ***** material, a paint, paper coating, and textile processing. Such an aqueous emulsion by adjusting the saponification degree of a PVA system polymer, Generally viscosity was low, it had the viscosity near a Newtonian flow, and the object for prizes has been carried out to various uses from what has the temperature dependence of emulsion viscosity high viscosity generally and comparatively small being comparatively obtained from a waterproof good thing. For example, as adhesives for woodwork, a hyperviscous emulsion is more preferred and the vinyl ester system aqueous emulsion which used what is called partial saponification PVA as protective colloid is used widely. While the vinyl ester system aqueous emulsion which used partial saponification PVA as protective colloid is excellent in freeze thaw stability and tends to obtain a hyperviscous thing, it has a problem inferior to a water resisting property. On the other hand, although the vinyl ester system aqueous emulsion which used full saponification PVA as protective colloid is excellent in a water resisting property, it has a problem inferior to low-temperature leaving stability. In order to solve such a problem JP,63-46252,A, Although making the compound which are 3-methyl-3-methoxybutanol and water solubility in JP,64-62347,A etc., and has an alcoholic OH radical contain is proposed and a water resisting property, leaving stability, etc. are improved, Since a water-soluble compound was blended, it was deficient in the plasticizing effect which there is a limit in the water resisting property, and becomes indispensable at a vinyl acetate system emulsion, and the actual condition was blending a certain plasticizer further. When such a compound is added, the degree of polymerization of the dispersoid of an emulsion, i.e., polyvinyl ester, falls by causing chain transfer during a polymerization. For this reason, there was a fault inferior to the adhesive strength at the time of being immersed in warm water etc. Using the vinyl alcohol system polymer containing an ethylene unit as a dispersing agent was proposed, and a water resisting property and low-temperature leaving stability have been improved substantially (JP,11-21529,A, JP,11-21380,A, JP,10-226774,A, etc.). However, when the vinyl alcohol system polymer containing an ethylene unit is also a full saponification article, surface activity is low compared with the conventional partial saponification PVA, and the particle diameter of the emulsion obtained becomes large. Since particle diameter became large, when an emulsion was coat-ized, there was a problem of being inferior to the transparency.

[0003]

[Problem(s) to be Solved by the Invention]This invention is a basis of such a situation and an object of this invention is to provide the vinylester resin emulsion which is excellent also in film formability and transparency, when it excels in a warm water-proof adhesive property and leaving stability and coat-izes further.

[0004]

[Means for Solving the Problem]A result of having repeated research wholeheartedly this invention persons developing a vinylester resin emulsion which has the aforementioned desirable character, an ethylene unit -- more than 0.5 mol % and less than 20 mol % -- a vinyl alcohol system polymer to contain being made into a dispersing agent, and, It finds out that a vinylester resin emulsion which obtained it by carrying out the emulsion polymerization of the vinyl ester system monomer under existence of a compound containing a sulfhydryl group is what satisfies the above-mentioned purpose, and came to complete this invention.

[0005]

[Embodiment of the Invention]the ethylene unit used for this invention -- more than 0.5 mol % and less than 20 mol % -- it contains -- a vinyl alcohol system polymer. It can obtain by there being no restriction in particular as a manufacturing method of (writing this polymer of this invention as a low ethylene denaturation PVA system polymer hereafter), and saponifying the copolymer of vinyl ester and ethylene by a publicly known method.

[0006]Although formic acid vinyl, vinyl acetate, vinyl propionate, vinyl pivalate, etc. are mentioned as vinyl ester, generally vinyl acetate is used preferably here.

[0007]What carried out copolymerization of the copolymerizable ethylenic unsaturated monomer in the range which does not spoil the effect of this invention may be sufficient as this dispersing agent. As such an ethylenic unsaturated monomer, For example, propylene, acrylic acid, methacrylic acid, fumaric acid, maleic acid (anhydrous), Itaconic acid, acrylonitrile, a methacrylonitrile, acrylamide, Methacrylamide, trimethyl (3-acrylamide 3-dimethylpropyl)-ammonium chloride, Acrylamide 2-methylpropanesulfonic acid and its sodium salt, Ethyl vinyl ether, butylvinyl ether, N-vinyl pyrrolidone, VCM/PVC, vinyl bromide, and vinyl fluoridation, a vinylidene chloride, vinylidene fluoride, N-vinylamide, such as tetrafluoroethylene, sodium vinylsulfonate, sodium allylsulfonate, N-vinyl pyrrolidone, N-vinylformamide, and N-vinylacetamide, is mentioned. Under existence of thiol compounds, such as thiol acetic acid and mercaptopropionic acid, copolymerization of the vinyl ester system monomers, such as vinyl acetate, can be carried out to ethylene, and the terminal modification thing obtained by saponifying it can also be used.

[0008]although the saponification degree in particular of the low ethylene denaturation PVA system polymer used as a dispersing agent in this invention is not restricted, the thing beyond 80 mol % is usually used -- desirable -- more than 85 mol % -- the thing beyond 95 mol % is used more preferably. When a saponification degree is less than [80 mol %], the concern to which the water solubility which is the original character of PVA falls arises. Although the degree of polymerization (viscosity average degree of polymerization) in particular of this low ethylene denaturation PVA system polymer is not restricted, the thing of the range of 100-8000 is usually used, and 300-3000 are used more preferably. When a degree of polymerization is less than 100, the feature as protective colloid of a low ethylene denaturation PVA system polymer is not demonstrated, but when exceeding 8000, there is a problem in industrial manufacture of this low ethylene denaturation PVA system polymer. It is important for the ethylene content in a low ethylene denaturation PVA system polymer that they are more than 0.5 mol % and less than 20 mol %. When an ethylene content does not satisfy this range, the purpose of above mentioned this invention cannot be attained.

[0009]Although the amount in particular of the low ethylene denaturation PVA system polymer used is not restricted, it is 1.5 to 7 weight section more preferably one to 10 weight section 0.5 to 15 weight section in the solid content 100 weight section of a vinylester resin emulsion. There is a possibility that polymerization stability may fall that the amount of the low ethylene denaturation PVA system polymer used is less than 0.5 weight sections. On the other hand, when 15 weight sections are exceeded, the concern to which the water resisting property of the vinylester resin emulsion obtained falls arises.

[0010]As a vinyl ester system monomer which constitutes the dispersoid of the vinylester resin emulsion of this invention, although formic acid vinyl, vinyl acetate, vinyl propionate, vinyl pivalate, etc. are mentioned, generally vinyl acetate is used preferably.

[0011]It is also one of the desirable modes to carry out copolymerization of a vinyl ester system monomer and the ethylene, and to consider it as an ethylene-vinylester resin emulsion in this invention. In that case, although the ethylene content in particular of an ethylene-vinylester resin emulsion is not restricted, 3 to 35% of the weight of a thing is usually used. By using the ethylene-vinylester resin emulsion of such an ethylene content, performances, such as a warm water-proof adhesive property, may improve further.

[0012]The above-mentioned dispersoid may carry out copolymerization of other copolymerizable ethylenic unsaturated monomers or diene system monomers in the range which does not spoil the effect of

this invention. As at least a kind of monomeric unit chosen from an ethylenic unsaturated monomer and a diene system monomer, Olefins [, such as propylene and isobutylene,], VCM/PVC, vinyl fluoridation. Halogenation olefins, such as vinylidenechloride and a vinylidene fluoride, Acrylic acid, methacrylic acid, methyl acrylate, ethyl acrylate, Butyl acrylate, 2-ethylhexyl acrylate, acrylic acid dodecyl, Acrylic ester, such as acrylic acid 2-hydroxyethyl, methyl methacrylate, Ethyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, Methacrylic acid ester, such as methacrylic acid dodecyl and methacrylic acid 2-hydroxyethyl, To acrylic acid dimethylaminoethyl, dimethylaminoethyl methacrylate and the fourth class ghosts of these, and a pan. Acrylamide, methacrylamide, N-methylolacrylamide, Styrene monomers, such as acrylamide system monomers, such as N,N'-dimethylacrylamide and acrylamide 2-methylpropanesulfonic acid and its sodium salt, styrene, alpha-methylstyrene, p-styrene sulfonic acid and sodium, and potassium salt, In addition, butadiene, such as N-vinyl pyrrolidone, isoprene, To diene system monomers, such as chloroprene, and a pan, divinylbenzene, tetra allyloxy ethane, N,N'-methylenebis acrylamide, 2,2'-bis(4-acryloxy polyethoxyphenyl)propane, 1,3-butylene-glycol diacrylate and 1,5-pentanediol diacrylate, Neopentyl glycol diacrylate, 1,6-hexanediol diacrylate, Diethylene glycol diacrylate, triethylene glycol diacrylate, Tetraethylene glycol diacrylate, polyethylene-glycol diacrylate, polypropylene-glycol diacrylate -- and, [pentaerythritol doria] Trimethylolpropane triacrylate, pentaerythritol tetraacrylate, Allyl methacrylate and 1,4-butanediol diacrylate, Ethylene glycol dimethacrylate, 1,3-butylene-glycol dimethacrylate, neopentyl glycol dimethacrylate, 1,6-hexanedioldimethacrylate, diethylene-glycol dimethacrylate, Triethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, Dipropylene glycol dimethacrylate, polypropylene-glycol dimethacrylate, Trimethylolethane trimethacrylate, trimethylolpropanetrimethacrylate, 2,2-bis(4-methacryloxy polyethoxyphenyl)propane, Methacrylic acid aluminum, methacrylic acid zinc, methacrylic acid calcium, Methacrylic acid magnesium, N, and N'-m-phenylene bis maleimide, Diallyl phthalate, triaryl cyanurate, triallyl isocyanurate, Polyfunctional monomers, such as triallyl trimellitate, diallyl chlarendate, and ethylene-glycol-diglycidyl-ether acrylate, are mentioned, independent, two or more sorts are mixed, and these are used.

[0013]Although not restricted especially as a compound containing the sulfhydryl group used when carrying out the emulsion polymerization of the vinyl ester system monomer of this invention, for example, 2-mercaptoethanol, 3-mercaptopropionic acid, n-dodecyl mercaptan, A thiophenol, the thioglycerol, 2-aminothiophenol, allyl mercaptan, 2-naphthalene thiol, 4-mercaptophenol, cystein, 2-mercaptobenzimidazole, thiactic acid, furfuryl mercaptan, Benzyl mercaptan, thiosalicylic acid, 2-aminothiophenol, etc. are mentioned, and 2-mercaptoethanol, 3-mercaptopropionic acid, n-dodecyl mercaptan, etc. are used especially preferably.

[0014]Although the addition in particular of the compound containing a sulfhydryl group is not restricted, it is 0.02 to 0.5 weight section preferably 0.01 to 1 weight section to solid content 100 weight section of a vinylester resin emulsion. The particle diameter of the emulsion from which an addition is obtained by less than 0.01 weight sections becomes large, and there is a possibility that a transparent coat may no longer be obtained. On the other hand, when one weight section is exceeded, there is concern to which polymerization stability falls.

[0015]Although the mean particle diameter in particular of the vinylester resin emulsion of this invention is not restricted, it is preferred that the measured value by dynamic light scattering is 1.3 micrometers or less, and it is usually 1 micrometer or less more preferably. When mean particle diameter is in this range, the transparency of the coat obtained from this emulsion becomes the more outstanding thing. The laser F-potential meter ELS-8000 grade by Otsuka Electronics Co., Ltd. can perform measurement by dynamic light scattering, for example.

[0016]Although the solid content in particular of the vinylester resin emulsion of this invention is not restricted, 40 to 65% of the weight of a thing is usually used preferably 30 to 70% of the weight. When solid content is less than 30 % of the weight, the leaving stability of an emulsion falls and there is a possibility of separating into two phases. When surpassing 70 % of the weight, the concern to which manufacture of a vinylester resin emulsion becomes difficult arises.

[0017]The process of the vinylester resin emulsion of this invention is not restricted in particular other than the focus of making the compound containing the sulfhydryl group of this invention contain, when carrying out the emulsion polymerization of the vinyl ester system monomer. For example, under existence of the compound which uses the solution of a PVA system polymer for a dispersing agent, and contains this sulfhydryl group in a reaction vessel, A vinyl ester system monomer is added temporarily or continuously, and the conventional method of adding and carrying out the emulsion polymerization of the polymerization initiators, such as peroxide system polymerization initiators, such as an azo polymerization initiator, hydrogen peroxide, ammonium persulfate, and potassium persulfate, is mentioned. In autoclave, in the case of an ethylene-vinylester resin emulsion, the solution of a low ethylene denaturation PVA system polymer is used for a dispersing agent, ethylene application of pressure is carried out, and the method of carrying out an emulsion polymerization is mentioned under existence of the compound containing a sulfhydryl group. Said polymerization initiator is used together

with a reducing agent, and may be used by a redox system. In that case, hydrogen peroxide is usually used with tartaric acid, L-ascorbic acid, a Rongalite, etc. Ammonium persulfate and potassium persulfate are used with sodium hydrogen sulfite, sodium bicarbonate, etc.

[0018] Although this emulsion obtained by the above-mentioned method can be used for it as it is, if the vinylester resin emulsion of this invention has necessity, it is a range which does not spoil the effect of this invention, and various publicly known emulsions can be conventionally added and used for it. To the vinylester resin emulsion of this invention, the additive agent by which normal use is carried out can be added. As an example of this additive agent, organic solvents, such as aromatic series, such as toluene and xylene, alcohols, ketone, ester species, and halogen containing solvents, a plasticizer, a suspending agent, a thickener, a fluidity improving agent, an antiseptic, a rust-proofer, a defoaming agent, a bulking agent, a wetting agent, colorant, etc. are mentioned. It is also possible to add an aluminium chloride, an aluminium nitrate and its hydrate, aluminum sulfate (sulfuric acid band), etc. furthermore.

[0019] The vinylester resin emulsion of this invention, Since it excels also in film formability and transparency when it excels in a warm water-proof adhesive property and leaving stability, especially elevated-temperature leaving stability and coat-sizes further, It is suitably used in fields, such as various adhesives, such as adhesives for woodwork, adhesives for paper making, a plywood / adhesives for vinyl chloride, the object for impregnated papers, the binder for nonwoven products, admixture, ***** material, a paint, paper coating and textile processing, and a coating agent.

[0020]

[Example] Next, an example and a comparative example explain this invention still in detail. A weight reference is meant unless it refuses especially a "part" and "%" in the following examples and comparative examples.

[0021] To example 1 reflux condenser, a dropping funnel, a thermometer, and the 1-l. glass polymerization vessels provided with the nitrogen blowing-in mouth. 279.2 copies of ion exchange water and polyvinyl alcohol (it outlines the following PVA)-1 (degree-of-polymerization 2000 and amount % of 3 mol of saponification degree % and ethylene denaturation of 97 mol) 19.5 copy were taught, and it dissolved thoroughly at 95 **. Next, 0.52 copy of n-dodecyl mercaptan was added after cooling this PVA solution. After carrying out temperature up to 60 **, having performed the nitrogen purge and agitating at 200 rpm, 4.4 copies and three copies of 5% hydrogen peroxide solution were prepared [the 10% solution of tartaric acid] after shot addition and for 26 copies of vinyl acetate, and the polymerization was started. The end of an initial polymerization was checked 30 minutes after the polymerization start. It cooled, after having gone over 0.9 copy and three copies of 5% hydrogen peroxide solution after shot addition, having gone over 234 copies of vinyl acetate in 2 hours, adding the 10% solution of tartaric acid continuously and completing a polymerization. Then, it filtered using the wire gauze made from stainless steel of 60 meshes. As for the above result, the polyvinyl acetate system emulsion of 47.6% of solids concentration was obtained. The various physical properties of this emulsion were measured by the following methods. A result is shown in Table 1.

(1) Warm water-proof adhesive strength (adhesion of a cover material); apply 150 g/m² of obtained vinylester resin emulsions to a cover material (straight wood grain), paste them together, and press by 7 kg/m² of load for 16 hours.

Then, it decompressed and it was recuperated for five days under 20 **65%RH.

This specimen was immersed in 70 ** warm water for 6 hours, and the compression shear strength was measured in the state where it has wetted wet. It was neglected in the dryer for 24 hours, and the connecting-and-disconnecting arrival intensity immediately after neglect which is not compressed was measured under 20 ** and 65%RH.

(2) Leaving stability; the emulsion was neglected during January at 60 **, and the state after neglect was observed. an evaluation result -- after O neglect -- change nothing and ** -- x as which thickening is regarded a little -- it gels, and is come out and shown.

(3) Coat transparency; the coat with a thickness of 500 micrometers which obtained the emulsion by carrying out cast film production at 20 ** was observed, and the transparency was evaluated. an evaluation result -- O -- almost -- transperance and ** -- a little -- nebula and x -- thoroughly, it becomes cloudy, and is come out and shown.

(4) Coat film formability; in 5 **, 0.5 g of emulsions were dropped on the slide glass, the state of the dry film was observed 24 hours afterward, and the following standards estimated. O transperance and ** -- a little -- nebula and x -- the mean particle diameter by the dynamic light scattering of the diameter; emulsion of nebula (5) emulsion particle was thoroughly measured using Otsuka Electronics ELS-8000.

(6) The degree of polymerization of a dispersoid; the degree of polymerization of the polyvinyl acetate which obtained the coat with a thickness of 500 micrometers which obtained the emulsion by carrying out cast film production at 20 ** by extracting it with acetone was measured by JISK6726.

(7) Emulsion viscosity : it measured at 30 **.

[0022] Instead of using n-dodecyl mercaptan used in example 2 Example 1, 2-mercaptoethanol was used, and also the emulsion polymerization as well as Example 1 was performed, and the polyvinyl acetate

system emulsion of 48% of solids concentration was obtained. Evaluation of this emulsion was performed like Example 1. A result is collectively shown in Table 1.

[0023]n-dodecyl mercaptan used in comparative example 1 Example 1 was not used, and also the emulsion polymerization as well as Example 1 was performed, and the polyvinyl acetate system emulsion of 47.5% of solids concentration was obtained. Evaluation of this emulsion was performed like Example 1. A result is collectively shown in Table 1.

[0024]Instead of adding at the time of an emulsion polymerization and using n-dodecyl mercaptan used in comparative example 2 Example 1, it blended after the emulsion polymerization, and also the emulsion polymerization as well as Example 1 was performed, and the polyvinyl acetate system emulsion of 47.6% of solids concentration was obtained. Evaluation of this emulsion was performed like Example 1. A result is collectively shown in Table 1.

[0025]Instead of using n-dodecyl mercaptan used in comparative example 3 Example 1, 2.6 copies of 3-methyl-3-methoxybutanol (SORUFITTO by Kuraray Co., Ltd.) was used, and also the emulsion polymerization as well as Example 1 was performed, and the polyvinyl acetate system emulsion of 47.8% of solids concentration was obtained. Evaluation of this emulsion was performed like Example 1. A result is collectively shown in Table 1.

[0026]PVA-2 (degree-of-polymerization 1000 and amount % of 8 mol of saponification degree % and ethylene denaturation of 99.2 mol) was used instead of using PVA-1 used in example 3 Example 1, and also the emulsion polymerization as well as Example 1 was performed, and the polyvinyl acetate system emulsion of 47.9% of solids concentration was obtained. Evaluation of this emulsion was performed like Example 1. A result is collectively shown in Table 1.

[0027]The nitrogen purge was performed, after teaching 72.7 copies of 5.5% solution of PVA-2, and 0.16 copy of n-dodecyl mercaptan to the resisting pressure autoclave provided with the example 4 nitrogen entrainment mouth, the thermometer, and the agitator and carrying out temperature up to 60 **. After teaching 80 copies of vinyl acetate, ethylene was pressurized to 40 kg/cm², two copies of hydrogen-peroxide-solution solutions and 0.3 copy of 2% Rongalite solution were pressed fit 0.5%, and the polymerization was started. In the place where residual vinyl acetate concentration became 10%, ethylene discharge was carried out, it was considered as ethylene pressure 20 kg/cm², 0.3 copy of hydrogen-peroxide-solution solution was pressed fit 3%, and the polymerization was completed. There is no condensation during a polymerization, it excels in polymerization stability, and 55.1% of solids concentration and the ethylene-vinyl acetate resin emulsion of 20 % of the weight of ethylene contents were obtained. Evaluation of this emulsion was performed like Example 1. A result is collectively shown in Table 1.

[0028]Tales doses of ion exchange water was used instead of using n-dodecyl mercaptan used in comparative example 4 Example 4, and also the emulsion polymerization as well as Example 6 was performed, and 55.2% of solids concentration and the ethylene-vinyl acetate resin emulsion of 20 % of the weight of ethylene contents were obtained. Evaluation of this emulsion was performed like Example 1. A result is collectively shown in Table 1.

[0029]it sets in the comparative example 5 Example 1 -- PVA-3 (PVA-217 by Kuraray Co., Ltd.; degree-of-polymerization 1700 and saponification degree % of 88 mol) was used instead of using PVA-1, and also the emulsion polymerization as well as Example 1 was performed, and the polyvinyl acetate system emulsion of 48% of solids concentration was obtained. Evaluation of this emulsion was performed like Example 1. A result is collectively shown in Table 1.

[0030]In comparative example 6 Example 1, PVA-4 (PVA-117 by Kuraray Co., Ltd.; degree-of-polymerization 1700 and saponification degree % of 98.5 mol) was used instead of using PVA-1, and also the emulsion polymerization as well as Example 1 was performed, and the polyvinyl acetate system emulsion of 47.9% of solids concentration was obtained. Evaluation of this emulsion was performed like Example 1. A result is collectively shown in Table 1.

[0031]

[Table 1]

	PVA	PVA量 %/固形分	添加剤 %/固形分	% /固形分	固形分 (%)	粒子径 (μ m)	エマルジョン粘度 (mPa·s)	エレン (wt%)	耐温水接着力 kg/cm ²	放置 安定性	皮膜 透明性	皮膜 造膜性	分散質 重合度
実施例1	PVA-1	7.5	n-ドデシルメルカプタン	0.2	47.6	1.0	5500	0	24	○	○	○	1580
実施例2	PVA-1	7.5	2-メルカプトエタノール	0.2	48	0.9	5000	0	23	○	○	○	1550
比較例1	PVA-1	7.5	なし	0	47.5	1.5	4500	0	17	△	△	△	1650
比較例2	PVA-1	7.5	n-ドデシルメルカプタンを後添	47.6	1.4	5000	0	17	△	△	△	△	1550
比較例3	PVA-1	7.5	ソルファイト	1	47.8	1.1	3500	0	13	○	○	○	800
実施例3	PVA-2	7.5	n-ドデシルメルカプタン	0.2	47.9	0.9	8000	0	28	○	○	○	1700
実施例4	PVA-2	5	n-ドデシルメルカプタン	0.17	55.1	0.9	3500	20	25	○	○	○	1780
比較例4	PVA-2	5	なし	0	55.2	1.5	3000	20	12	○	△	△	1700
比較例5	PVA-3	7.5	n-ドデシルメルカプタン	0.2	48	1.1	12000	0	0	○	○	○	1650
比較例6	PVA-4	7.5	n-ドデシルメルカプタン	0.2	47.9	1	2400	0	10	△	○	○	1550

[0032]PVA-1; degree-of-polymerization 2000, saponification degree % and ethylene-unit-content 3 mol %

PVA-2; degree of polymerization 1000 of 97 mol, and saponification degree [of 99.2 mol] %, ethylene-unit-content 8 mol %PVA-3; degree-of-polymerization 1700 and saponification degree % of 88 mol (PVA-217 by Kuraray Co., Ltd.)

PVA-4; degree-of-polymerization 1700 and saponification degree % of 98.5 mol (PVA-117 by Kuraray Co., Ltd.)

[0033]

[Effect of the Invention]The vinylester resin emulsion obtained by the method of this invention, Since it excels also in film formability and transparency when it excels in a warm water-proof adhesive property and leaving stability and coat-izes further, it is useful especially as various adhesives, and is suitably used in fields, such as the binder further for an impregnated paper and for nonwoven products, admixture, ***** material, a paint, paper coating, and textile processing.

[Translation done.]